Claims

1.) A polymerizable composition comprising

a) an ethylenically unsaturated monomer;

b) a radical polymerization initiator; and

c) a hydroxylamine, a nitrone or an alkyl N-oxid having a molecular weight of more than 250 g/mol.

2. A polymerizable composition aqccording to claim 1 wherein the ethylenically unsaturated monomer is selected from the group consisting of ethylene, propylene, n-butylene, i-butylene, styrene, substituted styrene, conjugated dienes, acrolein, vinyl acetate, vinylpyrrolidone, vinylimidazole, maleic anhydride, (alkyl)acrylic acidanhydrides, (alkyl)acrylic acid salts, (alkyl)acrylic esters, (alkyl)acrylonitriles, (alkyl)acrylamides, vinyl halides or vinylidene halides.

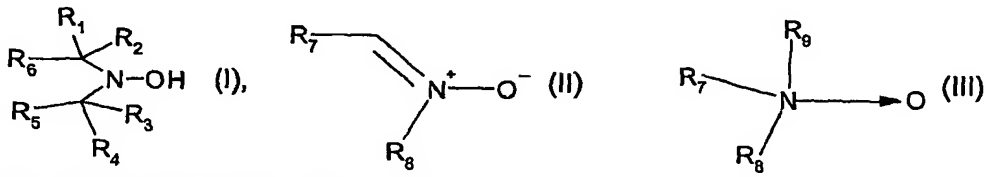
3. A polymerizable composition according to claim 1 wherein the ethylenically unsaturated monomer is a compound of formula $CH_2=C(R_a)-(C=Z)-R_b$, wherein Z is O or S;
R_a is hydrogen or C_1-C_4alkyl;
R_b is NH_2, $O^-(Me^+)$, glycidyl, unsubstituted C_1-C_{18}alkoxy, C_2-C_{100}alkoxy interrupted by at least one N and/or O atom, or hydroxy-substituted C_1-C_{18}alkoxy, unsubstituted C_1-C_{18}alkylamino, di(C_1-C_{18}alkyl)amino, hydroxy-substituted C_1-C_{18}alkylamino or hydroxy-substituted di(C_1-C_{18}alkyl)amino, $-O-CH_2-CH_2-N(CH_3)_2$ or $-O-CH_2-CH_2-N^+H(CH_3)_2$ An^-;
An^- is a anion of a monovalent organic or inorganic acid;
Me is a monovalent metal atom or the ammonium ion.

4. A polymerizable composition according to claim 2 wherein the ethylenically unsaturated monomer is styrene, n-butylacrylate, tert-butylacrylate, methylacrylate, ethylacrylate, propylacrylate, hexylacrylate or hydroxyethylacrylate.

5. A polymerizable composition according to claim 1 wherein the radical polymerization initiator is a azo compound, a peroxide, a perester or a hydroperoxide.

6. A polymerizable composition according to claim 5 wherein the radical polymerization initiator is a azo compound or a peroxide.

7. A polymerizable composition according to claim 1 wherein in component c) the hydroxylamine, the nitrone or the alkyl N-oxid having a molecular weight of more than 250 are of formulae (I), II) or (III)



R_1, R_2, R_3 and R_4 are independently hydrogen, phenyl or C_1-C_4alkyl;

R_5 and R_6 are independently C_7-C_{35}alkyl, C_7-C_{35}alkenyl or C_7-C_{35}alkinyl, which may be unsubstituted or substituted by phenyl, halogen, NH_2, $N(R_{21})_2$, -OH, -CN, $-NO_2$, or $-COOR_{21}$; or which may be interrupted by -O- or –C(O)-; or

R_5 and R_6 together are an alkylene bridge, which may be interrupted by a -O-, -C(O)- or a –N(C_1-C_{18}alkyl)- group to form a heterocyclic 5, 6, 7 or 8 membered ring, which may be further substituted by a $-O\text{-}C(O)\text{-}]_nR_{20}$, $NR_{21}\text{-}C(O)\text{-}]_nR_{20}$ or a ketal group;

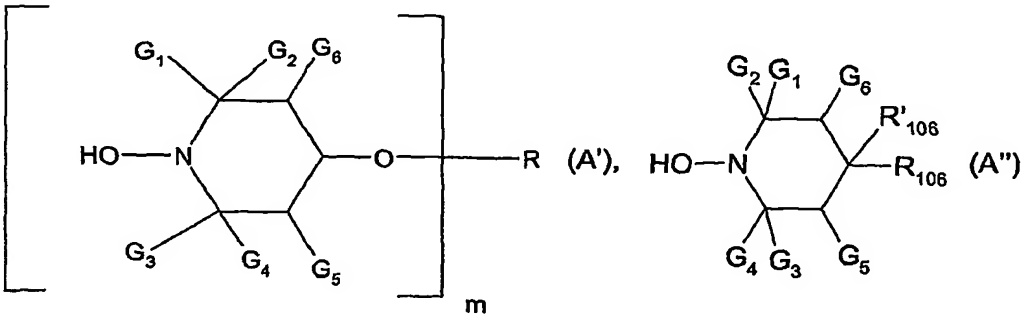
n is 1 or 2; wherein, when n is 1, R_{20} is hydrogen or C_1-C_{18}alkyl and, when n is 2, R_{20} is C_1-C_{18}alkylene; R_{21} is hydrogen or C_1-C_{18}alkyl;

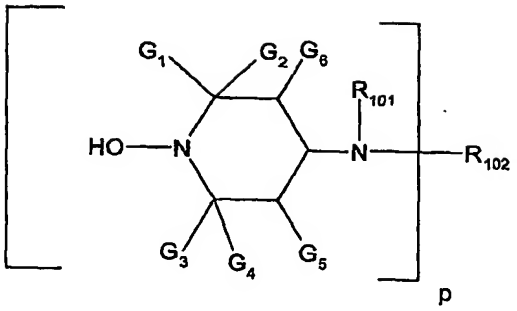
R_7 and R_8 are independently C_8-C_{36}alkyl; and

R_9 is C_1-C_4alkyl.

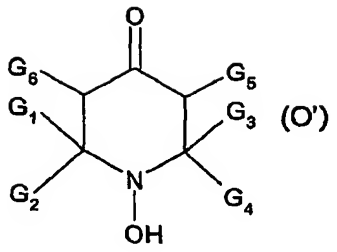
8. A polymerizable composition according to claim 7 wherein the hydroxylamine is of formula (I).

9. A polymerizable composition according to claim 7 wherein the compound of formula (I) is of formula A', A", B' or O'





(B') ,



(O')

wherein

m is 1,

R is hydrogen, C_1-C_{18}alkyl which is uninterrupted or interrupted by one or more oxygen atoms, cyanoethyl, benzoyl, glycidyl, a monovalent radical of an aliphatic carboxylic acid having 2 to 18 carbon atoms, of a cycloaliphatic carboxylic acid having 7 to 15 carbon atoms, or an α,β-unsaturated carboxylic acid having 3 to 5 carbon atoms or of an aromatic carboxylic acid having 7 to 15 carbon atoms;

p is 1;

R_{101} is C_1-C_{12}alkyl, C_5-C_7cycloalkyl, C_7-C_8aralkyl, C_2-C_{18}alkanoyl, C_3-C_5alkenoyl or benzoyl;

R_{102} is C_1-C_{18}alkyl, C_5-C_7cycloalkyl, C_2-C_8alkenyl unsubstituted or substituted by a cyano, carbonyl or carbamide group, or is glycidyl, a group of the formula $-CH_2CH(OH)-Z$ or of the formula -CO-Z or -CONH-Z wherein Z is hydrogen, methyl or phenyl;

R_6 and R'_6 together are both hydrogen, a group =O or $=N-O-R_{120}$ wherein

R_{120} is H, straight or branched C_1-C_{18}alkyl, C_3-C_{18}alkenyl or C_3-C_{18}alkinyl, which may be unsubstituted or substitued, by one or more OH, C_1-C_8alkoxy, carboxy, C_1-C_8alkoxycarbonyl; C_5-C_{12}cycloalkyl or C_5-C_{12}cycloalkenyl;

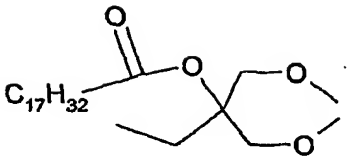
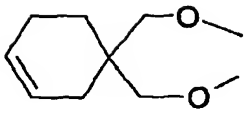
phenyl, C_7-C_9phenylalkyl or naphthyl which may be unsubstituted or substituted by one or more C_1-C_8alkyl, halogen, OH, C_1-C_8alkoxy, carboxy, C_1-C_8alkoxycarbonyl;

$-C(O)-C_1$-C_{36}alkyl, or an acyl moiety of a α,β-unsaturated carboxylic acid having 3 to 5 carbon atoms or of an aromatic carboxylic acid having 7 to 15 carbon atoms;

$-SO_3^-Q^+$, $-PO(O^-Q^+)_2$, $-P(O)(OR_2)_2$, $-SO_2-R_2$, $-CO-NH-R_2$, $-CONH_2$, $COOR_2$, or $Si(Me)_3$, wherein Q^+ is H^+, ammnonium or an alkali metal cation; or

R_{106} and R'_{106} are independently $-O-C_1$-C_{12}alkyl, $-O-C_3$-C_{12}alkenyl, $-O-C_3$-C_{12}alkinyl, $-O-C_5$-C_8cycloalkyl, -O-phenyl, -O-naphthyl, $-O-C_7$-C_9phenylalkyl; or

R_{106} and R'_{106} together form one of the bivalent groups $-O-C(R_{121})(R_{122})-CH(R_{123})-O-$, $-O-CH(R_{121})-CH_{122}-C(R_{122})(R_{123})-O-$, $-O-CH(R_{122})-CH_2-C(R_{121})(R_{123})-O-$, $-O-CH_2-C(R_{121})(R_{122})-CH(R_{123})-O-$, -O-o-phenylene-O-, -O-1,2-cyclohexyliden-O-,

-O-CH_2-CH=CH-CH_2-O-,  or  ; wherein

R_{121} is hydrogen, C_1-C_{12}alkyl, COOH, COO-(C_1-C_{12})alkyl or CH_2OR_{124};

R_{122} and R_{123} are independently hydrogen, methyl ethyl, COOH or COO-(C_1-C_{12})alkyl;

R_{124} is hydrogen, C_1-C_{12}alkyl, benzyl, or a monovalent acyl residue derived from an aliphatic, cycloaliphatic or aromatic monocarboxylic acid having up to 18 carbon atoms;

G_6 is hydrogen and G_5 is hydrogen or C_1-C_4alkyl, and

G_1, G_2, G_3 and G_4 are methyl; or

G_1 and G_3 are methyl and G_2 and G_4 are ethyl or propyl or G_1 and G_2 are methyl and G_3 and G_4 are ethyl or propyl.

10. A polymerizable composition according to claim 7 wherein in the hydroxylamine of formula (I)

R_1, R_2, R_3 and R_4 are hydrogen; and

R_5 and R_6 independently are C_7-C_{35}alkyl or C_7-C_{35}alkenyl.

11. A process for preparing an oligomer, a cooligomer, a polymer or a copolymer (block, random or graft) by free radical polymerization of at least one ethylenically unsaturated monomer or oligomer, which comprises (co)polymerizing the monomer or monomers/oligomers in the presence of

b) a free radical initiator and

c) a hydroxylamine, a nitrone or an alkyl N-oxid having a molecular weight of more than 250 g/mol.

12 A process according to claim 11 wherein the polymer obtained has a polydispersity of between 1.1 and 2.5.

13 A process according to claim 11 wherein the polymerization is carried out by heating and takes place at a temperature of between 70°C and 160°C.

14. A process according to claim 11 wherein the hydroxylamine, the nitrone or the alkyl N-oxid having a molecular weight of more than 250 g/mol is present in an amount of 0.001 to 10 mol % based on the monomer or monomers.

15. A process according to claim 11 wherein the weight ratio between the radical polymerization initiator and the hydroxylamine, the nitrone or the alkyl N-oxid having a molecular weight of more than 250 g/mol is from 1:5 to 5:1.

16. A polymer or copolymer obtainable by a process according to claim 11.

17. Use of a hydroxylamine, a nitrone or an alkyl N-oxid having a molecular weight of more than 250 for the controlled polymerization of ethylenically unsaturated monomers.